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NEWS 9	APR 28	EMBASE Controlled Term thesaurus enhanced
NEWS 10	APR 28	IMSRESEARCH reloaded with enhancements
NEWS 11	MAY 30	INPAFAMDB now available on STN for patent family searching
NEWS 12	MAY 30	DGENE, PCTGEN, and USGENE enhanced with new homology sequence search option
NEWS 13	JUN 06	EPFULL enhanced with 260,000 English abstracts
NEWS 14	JUN 06	KOREAPAT updated with 41,000 documents
NEWS 15	JUN 13	USPATFULL and USPAT2 updated with 11-character patent numbers for U.S. applications
NEWS 16	JUN 19	CAS REGISTRY includes selected substances from web-based collections
NEWS 17	JUN 25	CA/CAplus and USPAT databases updated with IPC reclassification data
NEWS 18	JUN 30	AEROSPACE enhanced with more than 1 million U.S. patent records
NEWS 19	JUN 30	EMBASE, EMBAL, and LEMBASE updated with additional options to display authors and affiliated organizations
NEWS 20	JUN 30	STN on the Web enhanced with new STN AnaVist Assistant and BLAST plug-in
NEWS 21	JUN 30	STN AnaVist enhanced with database content from EPFULL
NEWS 22	JUL 28	CA/CAplus patent coverage enhanced
NEWS 23	JUL 28	EPFULL enhanced with additional legal status information from the epoline Register
NEWS 24	JUL 28	IFICDB, IFIPAT, and IFIUDB reloaded with enhancements
NEWS 25	JUL 28	STN Viewer performance improved
NEWS 26	AUG 01	INPADOCDB and INPAFAMDB coverage enhanced
NEWS 27	AUG 13	CA/CAplus enhanced with printed Chemical Abstracts page images from 1967-1998
NEWS 28	AUG 15	CAOLD to be discontinued on December 31, 2008
NEWS 29	AUG 15	CAplus currency for Korean patents enhanced

NEWS EXPRESS JUNE 27 08 CURRENT WINDOWS VERSION IS V8.3,

AND CURRENT DISCOVER FILE IS DATED 23 JUNE 2008.

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FILE 'HOME' ENTERED AT 11:17:09 ON 18 AUG 2008

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STRUCTURE FILE UPDATES: 17 AUG 2008 HIGHEST RN 1041629-70-2
DICTIONARY FILE UPDATES: 17 AUG 2008 HIGHEST RN 1041629-70-2

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http://www.cas.org/support/stngen/stndoc/properties.html

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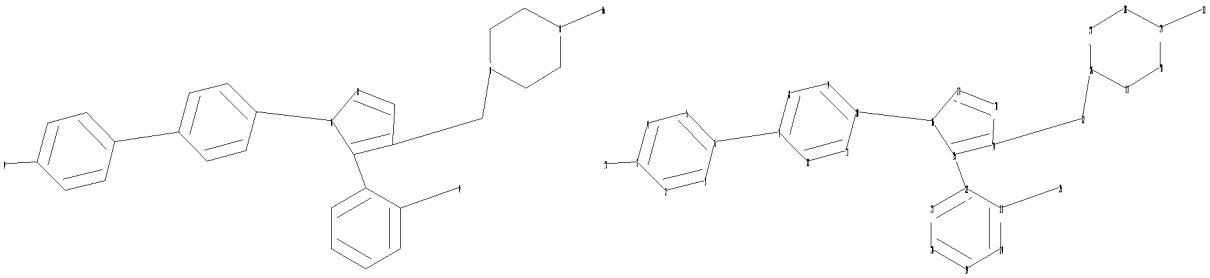

chain nodes :
13 25 32 33
ring nodes :
1 2 3 4 5 6 7 8 9 10 11 12 14 15 16 17 18 19 20 21 22 23 24
26 27 28 29 30 31
chain bonds :
3-13 6-7 10-16 14-32 15-22 23-25 26-32 29-33
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12 14-15 14-18
15-16 16-17 17-18 19-20 19-24 20-21 21-22 22-23 23-24 26-27 26-31 27-28
28-29 29-30 30-31
exact/norm bonds :
10-16 14-15 14-18 15-16 16-17 17-18 26-27 26-31 26-32 27-28 28-29 29-30
30-31
exact bonds :
3-13 6-7 14-32 15-22 23-25 29-33
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12 19-20 19-24
20-21 21-22 22-23 23-24

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:CLASS 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom
20:Atom 21:Atom 22:Atom 23:Atom 24:Atom 25:CLASS 26:Atom 27:Atom 28:Atom
29:Atom 30:Atom 31:Atom 32:CLASS 33:CLASS

L1 STRUCTURE UPLOADED

=> s l1 fam ful
FULL SEARCH INITIATED 11:17:45 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 89 TO ITERATE

100.0% PROCESSED 89 ITERATIONS 1 ANSWERS
SEARCH TIME: 00.00.01

L2 1 SEA FAM FUL L1

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=> file caplus
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                         ENTRY    SESSION
FULL ESTIMATED COST                                      70.11      70.32

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FILE COVERS 1907 - 18 Aug 2008  VOL 149 ISS 8
FILE LAST UPDATED: 17 Aug 2008  (20080817/ED)

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=> s l2
L3           1 L2

=> d l3 ibib abs

L3   ANSWER 1 OF 1  CAPLUS  COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER:        2004:841775  CAPLUS
DOCUMENT NUMBER:         141:350163
TITLE:                   Preparation of arylpyrazoles as serotonin 5-HT2A and
                         5-HT2C receptor antagonists
INVENTOR(S):             Schiemann, Kai; Ackermann, Karl-August; Arlt, Michael;
                         Finsinger, Dirk; Schadt, Oliver; Van Amsterdam,
                         Christoph; Bartoszyk, Gerd; Seyfried, Christoph
PATENT ASSIGNEE(S):      Merck Patent GmbH, Germany
SOURCE:                  Ger. Offen., 102 pp.
                         CODEN: GWXXBX
DOCUMENT TYPE:           Patent
LANGUAGE:                German
FAMILY ACC. NUM. COUNT:  1
PATENT INFORMATION:

     PATENT NO.          KIND   DATE        APPLICATION NO.         DATE
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     DE 10315572          A1    20041014    DE 2003-10315572        20030405
     AU 2004228120        A1    20041021    AU 2004-228120          20040308
     CA 2521201           A1    20041021    CA 2004-2521201         20040308
     WO 2004089931        A1    20041021    WO 2004-EP2353          20040308
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             CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
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GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,
NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
TD, TG

EP 1626967	A1	20060222	EP 2004-718277		20040308
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK					
BR 2004009164	A	20060411	BR 2004-9164		20040308
CN 1768051	A	20060503	CN 2004-80008572		20040308
JP 2006522035	T	20060928	JP 2006-504584		20040308
US 20060264419	A1	20061123	US 2005-552065		20051005
PRIORITY APPLN. INFO.:			DE 2003-10315572	A	20030405
			WO 2004-EP2353	W	20040308

OTHER SOURCE(S): MARPAT 141:350163
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Preparation of title compds. I [X = CH, N; R1 = H, halo, (CH2)nHet, etc.; R2 = (CH2)nHet, (CH2)nAr, cycloalkyl, etc.; R3, R4 = H, (CH2)nCOHet, CHO, etc.; n = 0-5; Ar = (un)substituted Ph; Het = (un)substituted monoarom., bicyclic-heterocycle] and their pharmaceutically acceptable salts were prepared For example, sodium triacetoxyborohydride meditated reductive amination of 1-methyl-piperazine and aldehyde II, e.g., prepared from 2-fluoro-α,γ-dioxo-benzenebutanoic Et ester in 4-steps, afforded the dihydrochloride salt of arylpyrazole III. In 5-HT2A receptor binding assays, 167-examples of compds. I exhibited IC50 values ranging from 0.015-4.7x10-7M. Compds. I are claimed suitable as ligands of 5-HT receptors.

=> file registry

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FULL ESTIMATED COST	3.39	73.71

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
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=> s l1 sss ful
FULL SEARCH INITIATED 11:18:30 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 163 TO ITERATE

100.0% PROCESSED 163 ITERATIONS 4 ANSWERS
SEARCH TIME: 00.00.01

L4 4 SEA SSS FUL L1

=> file caplus

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	178.36	252.07

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CA SUBSCRIBER PRICE	0.00	-0.80

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FILE COVERS 1907 - 18 Aug 2008 VOL 149 ISS 8
FILE LAST UPDATED: 17 Aug 2008 (20080817/ED)

Caplus now includes complete International Patent Classification (IPC)
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They are available for your review at:

http://www.cas.org/legal/infopolicy.html

=> s l4
L5 2 L4

=> d l5 ibib abs 1-2

L5 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:841775 CAPLUS
DOCUMENT NUMBER: 141:350163
TITLE: Preparation of arylpyrazoles as serotonin 5-HT2A and 5-HT2C receptor antagonists
INVENTOR(S): Schiemann, Kai; Ackermann, Karl-August; Arlt, Michael; Finsinger, Dirk; Schadt, Oliver; Van Amsterdam, Christoph; Bartoszyk, Gerd; Seyfried, Christoph
PATENT ASSIGNEE(S): Merck Patent GmbH, Germany
SOURCE: Ger. Offen., 102 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10315572	A1	20041014	DE 2003-10315572	20030405
AU 2004228120	A1	20041021	AU 2004-228120	20040308
CA 2521201	A1	20041021	CA 2004-2521201	20040308
WO 2004089931	A1	20041021	WO 2004-EP2353	20040308
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1626967	A1	20060222	EP 2004-718277	20040308
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK				
BR 2004009164	A	20060411	BR 2004-9164	20040308
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US 20060264419	A1	20061123	US 2005-552065	20051005
PRIORITY APPLN. INFO.:			DE 2003-10315572 A	20030405
			WO 2004-EP2353 W	20040308

OTHER SOURCE(S): MARPAT 141:350163
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Preparation of title compds. I [X = CH, N; R1 = H, halo, (CH2)nHet, etc.; R2 = (CH2)nHet, (CH2)nAr, cycloalkyl, etc.; R3, R4 = H, (CH2)nCOHet, CHO, etc.; n = 0-5; Ar = (un)substituted Ph; Het = (un)substituted monoarom., bicyclic-heterocycle] and their pharmaceutically acceptable salts were prepared For example, sodium triacetoxyborohydride meditated reductive amination of 1-methyl-piperazine and aldehyde II, e.g., prepared from 2-fluoro-α,γ-dioxo-benzenebutanoic Et ester in 4-steps, afforded the dihydrochloride salt of arylpyrazole III. In 5-HT2A receptor binding assays, 167-examples of compds. I exhibited IC50 values ranging from 0.015-4.7x10-7M. Compds. I are claimed suitable as ligands of 5-HT receptors.

L5 ANSWER 2 OF 2 CAPLUS

ACCESSION NUMBER: 2004:841772 CAPLUS
DOCUMENT NUMBER: 141:332186
TITLE: Preparation of arylpyrazoles as serotonin 5-HT2A and/or 5-HT2C receptor antagonists.
INVENTOR(S): Schadt, Oliver; Arlt, Michael; Finsinger, Dirk; Schiemann, Kai; Van Amsterdam, Christoph; Bartoszyk, Gerd; Seyfried, Christoph
PATENT ASSIGNEE(S): Merck Patent GmbH, Germany
SOURCE: Ger. Offen., 78 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10315569	A1	20041014	DE 2003-10315569	20030405
AU 2004228124	A1	20041021	AU 2004-228124	20040310
CA 2521227	A1	20041021	CA 2004-2521227	20040310
WO 2004089932	A1	20041021	WO 2004-EP2453	20040310
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RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1611122	A1	20060104	EP 2004-718926	20040310
EP 1611122	B1	20070613		
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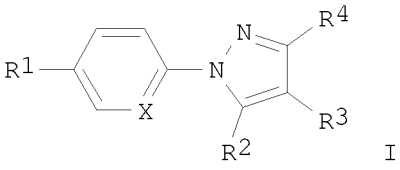
AT 364601	T	20070715	AT 2004-718926	20040310
ES 2287710	T3	20071216	ES 2004-718926	20040310
US 20070010531	A1	20070111	US 2005-552064	20051005

PRIORITY APPLN. INFO.: DE 2003-10315569 A 20030405
WO 2004-EP2453 W 20040310

OTHER SOURCE(S): MARPAT 141:332186
GI



I

AB Title compds. [I; R1 = H, A, halo, (CH2)nAr, cycloalkyl, CF3, NO2, cyano, C(NH)NOH, OCF3; R2 = (CH2)nHet, (CH2)nAr, cycloalkyl, CF3; R3, R4 = H, (CH2)nCO2R5, (CH2)nCOHet, CHO, (CH2)nOR5, (CH2)nHet, CH:NOA, etc.; R5 = H, A; A = alkyl, alkoxy, alkenyl, alkoxyalkyl; Ar = (substituted) Ph; Het = (aromatic) mono- or bicyclic heterocyclyl, heteroatom-containing organic residue; X

= N, CH; with provisos], were prepared Thus, [1-(4'-fluorobiphen-4-yl)-5-furan-2-yl-1H-pyrazol-4-ylmethyl]methyl(1-methylpyrrolidin-3-yl)amine showed 5-HT2A activity with IC50 = 5.14E-10.

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PASSWORD:
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NEWS 4	FEB 02	GENBANK enhanced with SET PLURALS and SET SPELLING
NEWS 5	FEB 06	Patent sequence location (PSL) data added to USGENE
NEWS 6	FEB 10	COMPENDEX reloaded and enhanced
NEWS 7	FEB 11	WTEXTILES reloaded and enhanced
NEWS 8	FEB 19	New patent-examiner citations in 300,000 CA/CAplus patent records provide insights into related prior art
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NEWS 11	FEB 23	MEDLINE now offers more precise author group fields and 2009 MeSH terms
NEWS 12	FEB 23	TOXCENTER updates mirror those of MEDLINE - more precise author group fields and 2009 MeSH terms
NEWS 13	FEB 23	Three million new patent records blast AEROSPACE into STN patent clusters
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NEWS 15	MAR 06	INPADOCDB and INPAFAMDB enhanced with new display formats
NEWS 16	MAR 11	EPFULL backfile enhanced with additional full-text applications and grants
NEWS 17	MAR 11	ESBIOBASE reloaded and enhanced
NEWS 18	MAR 20	CAS databases on STN enhanced with new super role for nanomaterial substances
NEWS 19	MAR 23	CA/CAplus enhanced with more than 250,000 patent equivalents from China
NEWS 20	MAR 30	IMSPATENTS reloaded and enhanced
NEWS 21	APR 03	CAS coverage of exemplified prophetic substances enhanced
NEWS 22	APR 07	STN is raising the limits on saved answers
NEWS 23	APR 24	CA/CAplus now has more comprehensive patent assignee information
NEWS 24	APR 26	USPATFULL and USPAT2 enhanced with patent assignment/reassignment information
NEWS 25	APR 28	CAS patent authority coverage expanded

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 NEWS 26  APR 28  ENCOMPLIT/ENCOMPLIT2 search fields enhanced
 NEWS 27  APR 28  Limits doubled for structure searching in CAS
                  REGISTRY
 NEWS 28  MAY 08  STN Express, Version 8.4, now available
 NEWS 29  MAY 11  STN on the Web enhanced
 NEWS 30  MAY 11  BEILSTEIN substance information now available on
                  STN Easy
 NEWS 31  MAY 14  DGENE, PCTGEN and USGENE enhanced with increased
                  limits for exact sequence match searches and
                  introduction of free HIT display format
 NEWS 32  MAY 15  INPADOCDB and INPAFAMDB enhanced with Chinese legal
                  status data

 NEWS EXPRESS MAY 26 09 CURRENT WINDOWS VERSION IS V8.4,
              AND CURRENT DISCOVER FILE IS DATED 06 APRIL 2009.

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  and other penalties.

* * * * * * * * * * * * * * * * STN  Columbus  * * * * * * * * * * * * * * * *

FILE 'HOME' ENTERED AT 11:03:14 ON 27 MAY 2009

=> file registry
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                         ENTRY    SESSION
FULL ESTIMATED COST                                       0.22       0.22

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STRUCTURE FILE UPDATES:   25 MAY 2009  HIGHEST RN 1149058-00-3
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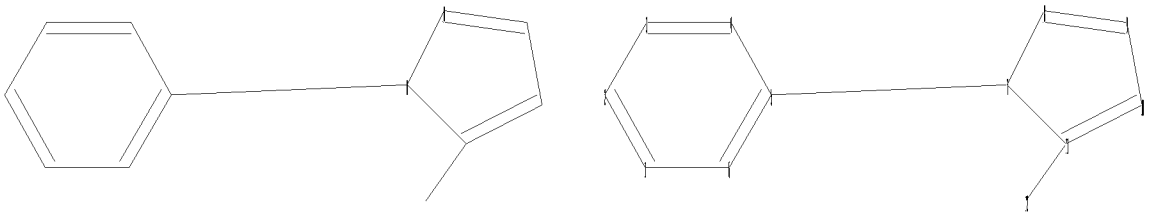

chain nodes :
12
ring nodes :
1 2 3 4 5 6 7 8 9 10 11
chain bonds :
5-7 11-12
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-11 8-9 9-10 10-11
exact/norm bonds :
5-7 7-8 7-11 8-9 9-10 10-11
exact bonds :
11-12
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:CLASS

L1   STRUCTURE UPLOADED

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FULL SEARCH INITIATED 11:03:43 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -   828790 TO ITERATE

100.0% PROCESSED   828790 ITERATIONS   434431 ANSWERS
SEARCH TIME: 00.00.12

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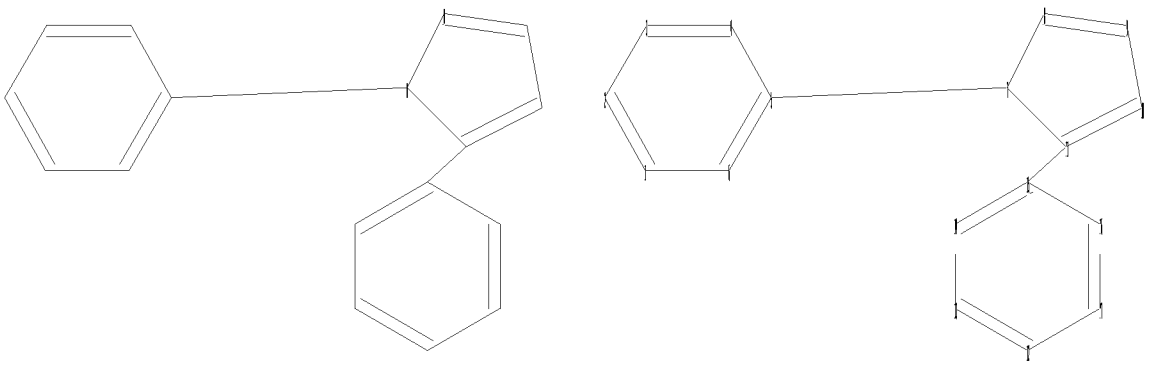

ring nodes :
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chain bonds :
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ring bonds :
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14-15 15-16 16-17
exact/norm bonds :
5-7 7-8 7-11 8-9 9-10 10-11
exact bonds :
11-15
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6 12-13 12-17 13-14 14-15 15-16 16-17

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:Atom 14:Atom 15:Atom 16:Atom 17:Atom

L3 STRUCTURE UPLOADED

=> s l3 fam ful
FULL SEARCH INITIATED 11:05:32 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 3064 TO ITERATE

100.0% PROCESSED 3064 ITERATIONS 2 ANSWERS
SEARCH TIME: 00.00.01

L4 2 SEA FAM FUL L3

=> file caplus
COST IN U.S. DOLLARS SINCE FILE ENTRY TOTAL SESSION
FULL ESTIMATED COST 260.17 260.39

FILE 'CAPLUS' ENTERED AT 11:05:41 ON 27 MAY 2009

FILE COVERS 1907 - 27 May 2009 VOL 150 ISS 22
FILE LAST UPDATED: 26 May 2009 (20090526/ED)
REVISED CLASS FIELDS (/NCL) LAST RELOADED: Feb 2009
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Feb 2009

CAplus now includes complete International Patent Classification (IPC)
reclassification data for the third quarter of 2008.

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This file contains CAS Registry Numbers for easy and accurate

=> s l4
L5   38 L4

=> d l5 ibib abs 1-38

L5   ANSWER 1 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2009:338987 CAPLUS
DOCUMENT NUMBER: 150:329777
TITLE: Copper-catalyzed C-H bond arylation of heterocyclic compounds and electron deficient arenes with aryl halides
INVENTOR(S):   Daugulis, Olafs; Do, Hien-Quang
PATENT ASSIGNEE(S):   The University of Houston System, USA
SOURCE: U.S. Pat. Appl. Publ., 112pp.
                         CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20090076266	A1	20090319	US 2008-208286	20080910
PRIORITY APPLN. INFO.:			US 2007-971466P P	20070911

OTHER SOURCE(S):   CASREACT 150:329777
AB   The present invention is a one-step method for efficiently converting carbon-hydrogen bonds into carbon-carbon bonds using a combination of aryl halides, a substrate, and a copper salt as catalyst. Thus, e.g., 2-phenylbenzoxazole was prepared in 93% yield by reacting benzoxazole with iodobenzene in the presence of a catalytic amount of copper(I) iodide and base in DMF with heating. This method allows faster introduction of complex mol. entities, a process that would otherwise require many more steps. This invention is particularly relevant for the organic synthesis of complex mols. such as, but not limited to, pharmacophores and explosives.

L5   ANSWER 2 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2008:1383562 CAPLUS
DOCUMENT NUMBER: 149:555078
TITLE: The Stille reaction
AUTHOR(S):   Farina, Vittorio; Krishnamurthy, Venkat; Scott, William J.
CORPORATE SOURCE: Boehringer Ingelheim Pharmaceuticals, Ridgefield, CT, USA
SOURCE: Organic Reactions (Hoboken, NJ, United States) (1997), 50, No pp. given
                         CODEN: ORHNBA
                         URL: http://www3.interscience.wiley.com/cgi-bin/mrwhome/107610747/HOME
PUBLISHER: John Wiley & Sons, Inc.
DOCUMENT TYPE: Journal; General Review; (online computer file)
LANGUAGE: English
OTHER SOURCE(S):   CASREACT 149:555078
AB   A review of the article The Stille reaction.

L5   ANSWER 3 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2008:1243395 CAPLUS

DOCUMENT NUMBER: 149:534179
TITLE: A General Method for Copper-Catalyzed Arylation of Arene C-H Bonds
AUTHOR(S): Do, Hien-Quang; Khan, Rana M. Kashif; Daugulis, Olafs
CORPORATE SOURCE: Department of Chemistry, University of Houston, Houston, TX, 77204-5003, USA
SOURCE: Journal of the American Chemical Society (2008), 130(45), 15185-15192
CODEN: JACSAT; ISSN: 0002-7863
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
AB A general method for copper-catalyzed arylation of sp2 C-H bonds with pKa's below 35 has been developed. The method employs aryl halide as the coupling partner, lithium alkoxide or K3PO4 base, and DMF, DMPU, or mixed DMF/xylenes solvent. A variety of electron-rich and electron-poor heterocycles such as azoles, caffeine, thiophenes, benzofuran, pyridine oxides, pyridazine, and pyrimidine can be arylated. Furthermore, electron-poor arenes possessing at least two electron-withdrawing groups on a benzene ring can also be arylated. Two arylcopper-phenanthroline complex intermediates were independently synthesized.
REFERENCE COUNT: 77 THERE ARE 77 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 4 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2007:554503 CAPLUS
DOCUMENT NUMBER: 147:143327
TITLE: Regioselective microwave-assisted synthesis of substituted pyrazoles from ethynyl ketones
AUTHOR(S): Bagley, Mark C.; Lubinu, M. Caterina; Mason, Christopher
CORPORATE SOURCE: School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK
SOURCE: Synlett (2007), (5), 704-708
CODEN: SYNLES; ISSN: 0936-5214
PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 147:143327
AB Reaction of α,β-ethynyl ketones and hydrazine derivs. gives 1,3- and 1,5-disubstituted pyrazoles in good yield. Microwave irradiation in concentrated HCl/MeOH (1.5% volume/volume), with concurrent cooling at sub-ambient temps. or at 120°, for 30 or 2 min, resp., facilitates rapid heterocyclization and preferentially gives the 1,3-disubstituted regioisomer.
REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 5 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2007:220868 CAPLUS
DOCUMENT NUMBER: 146:304597
TITLE: Electroluminescent organometallic complexes, organic electroluminescent devices, and displays and lightings using them
INVENTOR(S): Oshiyama, Tomohiro; Yasukawa, Noriko; Kato, Eisaku
PATENT ASSIGNEE(S): Konica Minolta Holdings, Inc., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 52pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2007051243	A	20070301	JP 2005-238536	20050819

PRIORITY APPLN. INFO.: JP 2005-238536 20050819
OTHER SOURCE(S): MARPAT 146:304597
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The electroluminescent organometallic complexes have partial structure of I (R01-R07 = H, substituent; ≥1 of R01, R03-R05, R07 = aromatic heterocyclic group; M01 = Group 8-10 metal). Also claimed are organometallic complexes having partial structures of I, wherein R01 or R05 represents an aromatic heterocyclic group. Also claimed are organometallic complexes of II (R2-R27 = H, substituent; R24 = aromatic heterocyclic group; X1-L1-X2 = bidentate ligand; X1, X2 = C, N; L1 = group of atoms; n2 = 1-3; m2 = 0-2; n2 + m2 = 2, 3; M21 = Group 8-10 metal). Organic electroluminescent (EL) devices with high emission efficiency and long life are provided with this invention.

L5 ANSWER 6 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2006:529471 CAPLUS
DOCUMENT NUMBER: 145:188781
TITLE: Palladium-catalyzed C-N bond formation: synthesis of 1-aryl-1H-pyrazoles from β-bromovinyl aldehydes and arylhydrazines
AUTHOR(S): Cho, Chan Sik; Patel, Daksha B.
CORPORATE SOURCE: Research Institute of Industrial Technology, Kyungpook National University, Taegu, 702-701, S. Korea
SOURCE: Tetrahedron (2006), 62(26), 6388-6391
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 145:188781
AB 1-Aryl-1H-pyrazoles and fused arylpyrazoles are prepared in 20-79% yields by cyclocondensation of arylhydrazines with cyclic and acyclic β-bromo-α,β-unsatd. aldehydes in the presence of palladium acetate, a diphosphine such as 1,1'-bis(diphenylphosphino)ferrocene (dppf), and sodium tert-butoxide in toluene at 125°.
REFERENCE COUNT: 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 7 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2006:202383 CAPLUS
DOCUMENT NUMBER: 145:489165
TITLE: Iodine(III) mediated synthesis of new 5-aryl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-1-phenylpyrazoles from dehydrogenation of 5-aryl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-1-phenylpyrazolines
AUTHOR(S): Prakash, Om; Kumar, Ajay; Kinger, Mayank; Singh, Shiv P.
CORPORATE SOURCE: Department of Chemistry, Kurukshetra University, Kurukshetra, 136 119, India
SOURCE: Indian Journal of Chemistry, Section B: Organic Chemistry Including Medicinal Chemistry (2006),

45B(2), 456-460
CODEN: IJSBDB; ISSN: 0376-4699
PUBLISHER: National Institute of Science Communication and Information Resources
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 145:489165
AB 3-Cinnamoyl-4-hydroxy-6-methyl-2-pyrones (chalcone analogs of DHA) on condensation with PhN2H3 in EtOH, yield 5-aryl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-1-phenylpyrazolines which undergo smooth dehydrogenation to the corresponding pyrazoles in good yield upon treatment with iodobenzene diacetate (IBD).
REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 8 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2005:1118021 CAPLUS
DOCUMENT NUMBER: 144:51499
TITLE: Regioselective Synthesis of 1-Aryl-3,4-substituted/annulated-5-(methylthio)pyrazoles and 1-Aryl-3-(methylthio)-4,5-substituted/annulated Pyrazoles
AUTHOR(S): Peruncheralathan, S.; Khan, T. A.; Ila, H.; Junjappa, H.
CORPORATE SOURCE: Department of Chemistry, Indian Institute of Technology, Kanpur, 208016, India
SOURCE: Journal of Organic Chemistry (2005), 70(24), 10030-10035
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 144:51499
AB Highly efficient and regioselective synthesis of 1-aryl-3,4-substituted/annulated-5-(methylthio)pyrazoles and 1-aryl-3-(methylthio)-4,5-substituted/annulated pyrazoles has been reported via cyclocondensation of arylhydrazines with either α-oxoketene dithioacetals or β-oxo dithio esters.
REFERENCE COUNT: 77 THERE ARE 77 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 9 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2002:855864 CAPLUS
DOCUMENT NUMBER: 139:214344
TITLE: Product class 1: pyrazoles
AUTHOR(S): Stanovnik, B.; Svete, J.
CORPORATE SOURCE: Faculty of Chemistry and Chemical Technology, Division of Organic Chemistry, Ljubljana, 61000, Slovenia
SOURCE: Science of Synthesis (2002), 12, 15-225
CODEN: SSCYJ9
PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal; General Review
LANGUAGE: English
AB A review. Methods for preparing pyrazoles are reviewed including cyclization, ring transformation, aromatization and substituent modifications.
REFERENCE COUNT: 909 THERE ARE 909 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 10 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2001:321317 CAPLUS
DOCUMENT NUMBER: 135:122152
TITLE: A complete model for the prediction of 1H- and 13C-NMR chemical shifts and torsional angles in phenyl-substituted pyrazoles
AUTHOR(S): Carrillo, J. R.; Cossio, F. P.; Diaz-Ortiz, A.; Gomez-Escalonilla, M. J.; de la Hoz, A.; Lecea, B.; Moreno, A.; Prieto, P.
CORPORATE SOURCE: Facultad de Quimica, Universidad de Castilla-La Mancha, Ciudad Real, 13071, Spain
SOURCE: Tetrahedron (2001), 57(19), 4179-4187
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB 1H- and 13C-NMR spectra of a number of N-phenyl- and C-phenylpyrazole derivs. have been obtained. The parameter most susceptible to changes in the dihedral angle is the difference δmeta-C-δortho-C. Values for this parameter have been determined and its usefulness for conformational studies of phenyl-substituted pyrazoles has been demonstrated. A correlation between torsional angles calculated by mol. mechanics and differences in 13C chemical shifts of the ortho and meta carbon atoms of the Ph groups in 29 N-phenyl-substituted pyrazole derivs. and 11 C-phenyl-substituted pyrazole derivs. has been found. For the N-phenyl-substituted derivs. a correlation between torsional angles and δmeta-H-δortho-H values has also been demonstrated. In all cases good correlations between angles and differences in chemical shifts were observed
REFERENCE COUNT: 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 11 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2000:500201 CAPLUS
DOCUMENT NUMBER: 133:281725
TITLE: A New Germanium-Based Linker for Solid Phase Synthesis of Aromatics: Synthesis of a Pyrazole Library
AUTHOR(S): Spivey, Alan C.; Diaper, Christopher M.; Adams, Harry; Rudge, Andrew J.
CORPORATE SOURCE: Department of Chemistry, University of Sheffield, Yorkshire, S3 7HF, UK
SOURCE: Journal of Organic Chemistry (2000), 65(17), 5253-5263
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 133:281725
AB An efficient synthesis of chlorogermane linker 4-HOC6H4CH2CH2GeMe2Cl (I) is described. Economic introduction of germanium into this linker is accomplished by insertion of dichlorogermylene [from germanium(IV) chloride] into the homobenzylic C-Cl bond of 4-HOC6H4CH2CH2Cl. Using linker I, transmetalation with lithiated 4-acetophenone, 3-acetophenone, and 4-methoxybiphenyl followed by Mitsunobu-type coupling to Argogel gives functionalized resins. Treatment of resin-bound 4-HOC6H4CH2CH2GeMe2C6H4(C6H4OMe-4)-4 with TFA, ICl, Br2, or NCS effects clean ipso-degermylation releasing 4-MeOC6H4C6H4R-4 [R = H, I, Br, Cl]. Resin-bound 4-HOC6H4CH2CH2GeMe2C6H4R1 [R1 = 4-Ac, 3-Ac] are employed for the parallel synthesis of a library of pyrazoles by enaminone formation (using Bredereck's reagent), condensative ring-closure (using a series of monosubstituted hydrazines), and cleavage (using TFA and Br2). Anal. of this library reveals the influence of the hydrazine substituent on both the regioselectivity of ring-closure and the propensity for electrophilic substitution at the 4-position of the pyrazoles during ipso-degermylative

cleavage.
REFERENCE COUNT: 96 THERE ARE 96 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 12 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1997:57955 CAPLUS
DOCUMENT NUMBER: 126:211777
ORIGINAL REFERENCE NO.: 126:40951a
TITLE: Substituent effects on the 15N NMR parameters of azoles
AUTHOR(S): Claramunt, Rosa Maria; Sanz, Dionisia; Lopez, Concepcion; Jimenez, Jose Antonio; Jimeno, Maria Luisa; Elguero, Jose; Fruchier, Alain
CORPORATE SOURCE: Departamento de Quimica Organica y Biologia, Facultad de Ciencias, UNED, Madrid, E-28040, Spain
SOURCE: Magnetic Resonance in Chemistry (1997), 35(1), 35-75
CODEN: MRCHEG; ISSN: 0749-1581
PUBLISHER: Wiley
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The 15N chemical shifts and a large collection of coupling consts. pertaining to azoles have been gathered from the literature. To complete this collection and to check some anomalies, the spectra of 14 compds. in several solvents were recorded again and 31 compds. were studied for the first time; in all, data for 420 compds. (pyrroles, imidazoles, pyrazoles, triazoles, tetrazoles, indoles, benzimidazoles, indazoles, benzotriazoles and carbazoles) are reported. Additive models are used to discuss the substituent chemical shifts.
REFERENCE COUNT: 52 THERE ARE 52 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 13 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1992:425806 CAPLUS
DOCUMENT NUMBER: 117:25806
ORIGINAL REFERENCE NO.: 117:4639a,4642a
TITLE: Carbon-13 chemical shifts and proton-13C coupling constants of N-phenyl-, N-p-fluorophenyl- and N-o-nitrophenylpyrazoles
AUTHOR(S): Begtrup, Mikael; Vedsoe, Per; Cabildo, Pilar; Claramunt, Rosa Maria; Elguero, Jose; Meutermans, Wim
CORPORATE SOURCE: Dep. Org. Chem., R. Dan. Sch. Pharm., Copenhagen, DK-2100, Den.
SOURCE: Magnetic Resonance in Chemistry (1992), 30(5), 455-9
CODEN: MRCHEG; ISSN: 0749-1581
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The 13C chemical shifts and some 1H-13C coupling consts. of twelve N-arylpyrazoles are reported. The assignments were made by using the effects of a fluorine substituent and two-dimensional techniques.

L5 ANSWER 14 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1988:528890 CAPLUS
DOCUMENT NUMBER: 109:128890
ORIGINAL REFERENCE NO.: 109:21473a,21476a
TITLE: Reaction of 2-dimethylaminomethylene-1,3-diones with dinucleophiles. VI. Synthesis of ethyl or methyl 1,5-disubstituted 1H-pyrazole-4-carboxylates
AUTHOR(S): Menozzi, Giulia; Mosti, Luisa; Schenone, Pietro
CORPORATE SOURCE: Ist. Sci. Farm., Univ. Genoa, Genoa, 16132, Italy
SOURCE: Journal of Heterocyclic Chemistry (1987), 24(6), 1669-75
CODEN: JHTCAD; ISSN: 0022-152X

DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 109:128890
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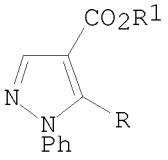

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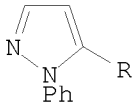
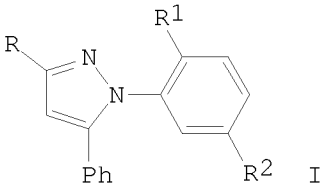


III

AB Reaction of RCOCH2CO2R1 (R = alkyl, Ph, PhCH2; R1 = Me, Et) with N,N-dimethylformamide di-Me acetal gave, generally in excellent yields, RCOC(:CHNMe2)CO2R1 (I) which reacted with phenylhydrazine to afford the esters (II) of 5-substituted 1-phenyl-1H-pyrazole-4-carboxylic acids in high yields. Ester II were hydrolyzed to 5-substituted 1-phenyl-1H-pyrazole-4-carboxylic acids which were converted by heating to 5-substituted 1-phenyl-1H-pyrazoles III in excellent yields. Reaction of I with methylhydrazine afforded in general a mixture of 3- and 5-substituted Et 1-methyl-1H-pyrazole-4-carboxylates with the exception of I (R = PhCH2, R1 = Me), which gave in high yield Me 5-benzyl-1-methyl-1H-pyrazole-4-carboxylate, which was hydrolyzed to the corresponding pyrazolecarboxylic acid. This afforded by heating 5-benzyl-1-methyl-1H-pyrazole in quant. yield.

L5 ANSWER 15 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1988:186642 CAPLUS
DOCUMENT NUMBER: 108:186642
ORIGINAL REFERENCE NO.: 108:30667a,30670a
TITLE: Oxidative cyclization of arylhydrazones of chalcones and benzalacetones to pyrazoles by thianthrene cation radical
AUTHOR(S): Kovelesky, Albert C.; Shine, Henry J.
CORPORATE SOURCE: Dep. Chem. Biochem., Texas Tech Univ., Lubbock, TX, 79409, USA
SOURCE: Journal of Organic Chemistry (1988), 53(9), 1973-9
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 108:186642
GI

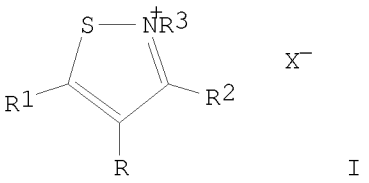


I

AB Phenyl-, (p-nitrophenyl)-, and (2,4-dinitrophenyl)hydrazones of chalcone (benzalacetophenone), benzalacetone, and of some of their derivs. undergo oxidative cyclization in reaction with thianthrene cation radical perchlorate. The products are, e.g., 1,3,5-triaryl- (I; R = Ph; R1, R2 = H, NO2) and 3-methyl-1,5-diarylpyrazoles (I; R = Me; R1, R2 = H, NO2) and

are formed in excellent yields. Cyclization appears to occur by way of the arylhydrazone cation radical and not via the preliminary, acid-catalyzed formation of the corresponding pyrazoline.

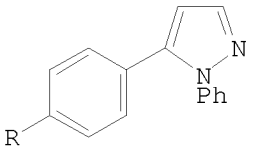
L5 ANSWER 16 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1985:596029 CAPLUS
DOCUMENT NUMBER: 103:196029
ORIGINAL REFERENCE NO.: 103:31589a,31592a
TITLE: The reactions of isothiazolium salts with nitrogen nucleophilic reagents
AUTHOR(S): Hassan, Mohamed E.; Magraby, M. A.; Aziz, Magda A.
CORPORATE SOURCE: Chem. Dep., Aswan Univ., Aswan, Egypt
SOURCE: Tetrahedron (1985), 41(10), 1885-91
CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 103:196029
GI



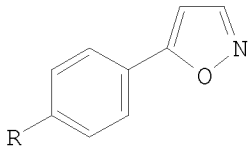
I

AB Isothiazolium salts I (R = R1 = H, R2 = Ph, R3 = Me, Ph, X = ClO4; R = H, R1 = SMe, R2 = Ph, R3 = Me, X = ClO4; R = H, R1 = Ph, R2 = SMe, R3 = Me, X = iodide; R = R2 = H, R1 = Ph, R3 = Me; X = ClO4; R = Ph, C6H4Me-p, R1 = R2 = H, R3 = Me, X = ClO4) reacted with a number of N nucleophiles including NH3, PhNHNH2, H2NOH and PhCH2NH2. The products obtained suggest that the position of initial nucleophilic attack is at the S of the heterocyclic cation.

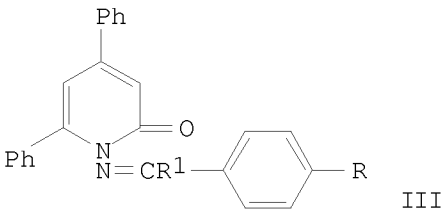
L5 ANSWER 17 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1984:530627 CAPLUS
DOCUMENT NUMBER: 101:130627
ORIGINAL REFERENCE NO.: 101:19873a,19876a
TITLE: New synthesis of pyrazole and isoxazole derivatives
AUTHOR(S): Molina, P.; Fresneda, P. M.
CORPORATE SOURCE: Fac. Cienc., Univ. Murcia, Murcia, Spain
SOURCE: Journal of Heterocyclic Chemistry (1984), 21(2), 461-4
CODEN: JHTCAD; ISSN: 0022-152X
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 101:130627
GI



I



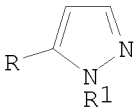
II



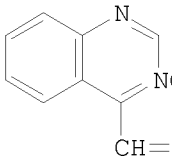
III

AB 1-Phenylpyrazoles I (R = H, Me, NO2, MeO, Br, Cl) and isoxazoles II were prepared by treating ketimines III (R1 = Me) with (MeO)2CHNMe2 to give enaminimines III (R1 = CH:CHNMe2) which were cyclocondensed with PhNHNH2 or H2NOH.HCl.

L5 ANSWER 18 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1980:604527 CAPLUS
DOCUMENT NUMBER: 93:204527
ORIGINAL REFERENCE NO.: 93:32633a,32636a
TITLE: Reaction of activated methyl groups with N,N-dimethylformamide dialkyl acetals
AUTHOR(S): Tisler, M.; Stanovnik, B.; Vercek, B.
CORPORATE SOURCE: Dep. Chem., Univ. Ljubljana, Ljubljana, 61000, Yugoslavia
SOURCE: Vestnik Slovenskega Kemijskega Drustva (1980), 27(1), 65-72
CODEN: VSKDAA; ISSN: 0560-3110
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 93:204527
GI



II



III

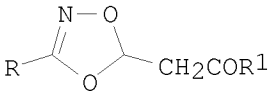
AB RCOCH:CHNMe2 (I, R = 2-pyridyl, 3-pyridyl, 2-O2NC6H4) were prepared in 49-73% yield by treating RAc with Me2NCH(OMe)2. The pyrazoles II (R1 = H, Ph) were obtained by treating I with R1NHNH2. II (R = R1 = Ph) was similarly obtained from BzCH:CHNMe2. The quinazoline oxide III was prepared in 56% yield by treating 2-H2NC6H4CMe:NOH with Me2NCH(OEt)2.

L5 ANSWER 19 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1980:41480 CAPLUS
DOCUMENT NUMBER: 92:41480
ORIGINAL REFERENCE NO.: 92:6913a,6916a
TITLE: Reactivity of α-halogenated imino compounds. Part XVIII. Reactivity of

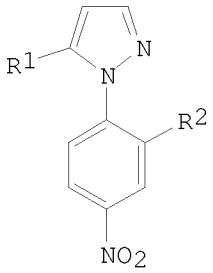
N-aryl-α,α-dichlorinated arylketimines
AUTHOR(S): De Kimpe, Norbert; Verhe, Roland; De Buyck, Laurent; Tukiman, Sunari; Schamp, Niceas
CORPORATE SOURCE: Lab. Org. Chem., State Univ. Gent, Ghent, Belg.
SOURCE: Tetrahedron (1979), 35(6), 789-98
CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 92:41480

AB E-RCCl2C(C6H4R1-4):NC6H4R2 (I; R = alkyl, R1 = H, Br, R2 = H, Me, OMe) were prepared by chlorination of E-RCH2C(C6H4R1-4):NC6H4R2 by N-chlorosuccinimide in CCl4. I (R = Me)(R1 = H, R2 = H, p-Me, m-Me, p-OMe; R1 = Br, R2 = H) with NaOMe/MeOH, followed by acid hydrolysis, gave 4-R1C6H4COCOMe, 4-R1C6H4COC(OMe):CH2, and 4-R1C6H4COCH:CHNHC6H4R2, formation of the latter formally involving a migration of N from C-1 to C-3. More highly substituted I with NaOMe/MeOH gave mainly α-chloro-α,β-unsatd. ketones. With long-chain I, a formal γ-functionalization was observed Reaction mechanisms are discussed in detail.

L5 ANSWER 20 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1978:190700 CAPLUS
DOCUMENT NUMBER: 88:190700
ORIGINAL REFERENCE NO.: 88:29989a
TITLE: 2-(Acylmethyl)-1,3,4-dioxazoles by ketovinylation of hydroxamic acids
AUTHOR(S): Schroth, Werner; Peters, Olaf
CORPORATE SOURCE: Sekt. Chem., Martin-Luther-Univ., Halle/Saale, Ger. Dem. Rep.
SOURCE: Zeitschrift fuer Chemie (1978), 18(2), 57-8
CODEN: ZECEAL; ISSN: 0044-2402
DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 88:190700
GI



II



AB Hydroxamic acids RCONHOH reacted with β-chlorovinyl ketones R1COCH:CHCl to give 21-96% of the dioxazoles I (R = Ph, styryl, 4-O2NC6H4, CH2Cl; R1 = Me, Me2CH, Ph, 4-ClC6H4, 4-O2NC6H4, o-tolyl). I were hydrolyzed by alc. alkali to hydroxamic acids and the corresponding β-dicarbonyl compds. Reaction of I with 2,4-R2(O2N)C6H3NHNH2 (R2 = H, NO2) gave the pyrazoles II (R1 and R2 as above).

L5 ANSWER 21 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1976:17219 CAPLUS
DOCUMENT NUMBER: 84:17219
ORIGINAL REFERENCE NO.: 84:2851a,2854a
TITLE: Intermediates isolated during the synthesis of 1,3-

and 1,5-diphenylpyrazoles
AUTHOR(S): Rull, Thomas; Le Strat, Georges
CORPORATE SOURCE: Cent. Rech. ATO Chim., Orsay, Fr.
SOURCE: Bulletin de la Societe Chimique de France (1975), (5-6, Pt. 2), 1375-9
CODEN: BSCFAS; ISSN: 0037-8968
DOCUMENT TYPE: Journal
LANGUAGE: French
OTHER SOURCE(S): CASREACT 84:17219
GI For diagram(s), see printed CA Issue.
AB BzCH:CHNHNHPh, and pyrazolines I (R = Ph, R1 = H; R = H, R1 = Ph) were isolated as intermediates in the reaction of BzCH2CHO with PhNHNH2 to give title diphenylpyrazoles. Reaction of BzCH:CHOBz with PhNHNH2 gave BzCH:CHNPhNH2 as the intermediate to 1,3-diphenylpyrazole. Reaction of BzCH2CHO with PhNHNHCHO gave BzCH:CHNPhNHCHO, which gave 1,3- and 1,5-diphenylpyrazoles in 77.5:22.5 ratio and 82% yield.

L5 ANSWER 22 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1971:420283 CAPLUS
DOCUMENT NUMBER: 75:20283
ORIGINAL REFERENCE NO.: 75:3247a,3250a
TITLE: Sulfurated organic compounds. VIII. Reaction of phenylhydrazine with 3-aryl-1,2-dithiolylium bisulfates and 3,5-diaryl-1,2-dithiolylium perchlorates. 3-Aryl-1-phenylpyrazoles, 5-aryl-1-phenylpyrazoles, and 3,5-diaryl-1-phenylpyrazoles
AUTHOR(S): Bergeon, Marie T.; Metayer, Claire; Quiniou, Herve
CORPORATE SOURCE: Fac. Sci., Nantes, Fr.
SOURCE: Bulletin de la Societe Chimique de France (1971), (3), 917-24
CODEN: BSCFAS; ISSN: 0037-8968
DOCUMENT TYPE: Journal
LANGUAGE: French
GI For diagram(s), see printed CA Issue.
AB PhNHNH2 (I) and 3-aryl dithioles (II) reacted to give 2 pyrazole isomers (III) which were separated by Al2O3 chromatog. Thus, II (R = Ph, R1 = H, X = HSO4) reacted with I in EtOH to give III (R = Ph, R1 = H) (major) and III (R = H, R1 = Ph). II (R = R1 = Ph, X = ClO4) reacted with I to give 60% III (R = R1 = Ph). II (R = Ph, R1 = p-ClC6H4, X = ClO4) when treated similarly gave the isomeric III (R = Ph, R1 = p-ClC6H4) (major) and III (R = p-ClC6H4, R1 = Ph). The structure of pyrazoles was determined from chemical anal. and NMR spectra.

L5 ANSWER 23 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1971:99117 CAPLUS
DOCUMENT NUMBER: 74:99117
ORIGINAL REFERENCE NO.: 74:16133a,16136a
TITLE: Investigations on pyrazole derivatives. V. Uv absorption spectra of derivatives of 6H,7H-pyrazolo[3,2-b][1,2,4]thiazole and some pyrazole derivatives
AUTHOR(S): Dymek, Wojciech; Ryznerski, Zygmunt
CORPORATE SOURCE: Dep. Pharm. Chem., Med. Acad., Cracow, Pol.
SOURCE: Dissertationes Pharmaceuticae et Pharmacologicae (1970), 22(6), 419-25
CODEN: DPHFAK; ISSN: 0012-3870
DOCUMENT TYPE: Journal
LANGUAGE: English
GI For diagram(s), see printed CA Issue.
AB The uv absorption spectra of substituted 6H,7H-pyrazolo[3,2-b][1,2,4]thiadiazoles (I) exhibited a bathochromic shift and a change in extinction coefficient in comparison with the spectra of the

corresponding pyrazole derivs. The most pronounced changes in the maxima positions are produced by substituents at position 7 in I and at position 4 in pyrazole. Substituents at other positions caused little change in the maxima position but did influence the intensity.

L5 ANSWER 24 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1970:132597 CAPLUS
DOCUMENT NUMBER: 72:132597
ORIGINAL REFERENCE NO.: 72:23735a,23738a
TITLE: Azoles. LXIII. Reactions of mono- and 1,2-disubstituted hydrazines with α-acetylenic carbonyl compounds
AUTHOR(S): Coispeau, Gerard; Elguero, Jose; Jacquier, Robert
CORPORATE SOURCE: Lab. Syn. Etude Phys.-Chim. Heterocycles Azotes, Fac. Sci., Montpellier, Fr.
SOURCE: Bulletin de la Societe Chimique de France (1970), (2), 689-96
CODEN: BSCFAS; ISSN: 0037-8968
DOCUMENT TYPE: Journal
LANGUAGE: French
AB The reactions of MeNHNH2, PhNHNH2, and 2,4-dinitrophenyl-hydrazine with α-acetylenic carbonyls such as HC.tplbond.CCH(OEt)2 (i.e., acetals were used when the aldehydes were unstable), HC.tplbond.CAc, HC.tplbond.CBz, and PhC.tplbond.CAc gave N-substituted-pyrazoles. The reactions of MeNHNHPh with the same carbonyls in the presence of HI gave the corresponding pyrazolium iodides. Contrary to analogous condensations with β-diketones, the orientation of the reaction permits the preparation of certain isomers which are difficult to prepare

L5 ANSWER 25 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1968:512873 CAPLUS
DOCUMENT NUMBER: 69:112873
ORIGINAL REFERENCE NO.: 69:21119a,21122a
TITLE: Polarographic study of derivatives of Δ2-pyrazoline
AUTHOR(S): Shimanskaya, N. P.; Buryakovskaya, E. G.; Bezuglyi, V. D.; Tsukerman, S. V.
CORPORATE SOURCE: Vses. Nauch.-Issled. Inst. Monokrist., Kharkov, USSR
SOURCE: Zhurnal Obshchei Khimii (1968), 38(8), 1676-9
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Russian
AB Polarographic data are presented, mainly graphically, for 14 examples of 2-pyrazolines with a 1-phenyl substituent and substituents in 3- and 5-positions selected from Ph, H, 2-furyl, 2-selenophene-yl, p-dimethylaminophenyl, 2-thienyl, p-anisyl, 2,4-dimethoxyphenyl, Me, and p-ClC6H4. Substituents in the 3-position affect the half-wave potentials materially and the declining potentials follow the rise in electron-acceptor capability of these groups in order: 2-furyl, 2-thienyl, 2-selenophene-yl. Substituents in the 5-position exert only their inductive effects. The half-wave potentials were readily correlated with the absorption spectral long-wavelength maximum of each compound with the wavelength of the band declining linearly with rising neg. value of the half-wave potential.

L5 ANSWER 26 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1968:451379 CAPLUS
DOCUMENT NUMBER: 69:51379
ORIGINAL REFERENCE NO.: 69:9579a,9582a
TITLE: Molecular orbital calculations of pyrazoles. I. Alkyl- and aryl-pyrazoles
AUTHOR(S): Finar, I. L.

CORPORATE SOURCE: Northern Polytech., London, UK
SOURCE: Journal of the Chemical Society [Section] B: Physical Organic (1968), (7), 725-32
CODEN: JCSPAC; ISSN: 0045-6470
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The longest $\pi \rightarrow \pi^*$ wave absorption band in the uv spectra of 40 alkyl- and arylpyrazoles was calculated by the simple L.C.A.O.M.O. method. With a suitable choice of parameters, a good correlation was obtained between the calculated and observed frequencies. Angles of twist were calculated for some sterically hindered pyrazoles, and the stabilities of some tautomeric forms of 1-unsubstituted pyrazoles and the basicities of a number of pyrazoles were examined Electrophilic and homolytic substitution in pyrazole, 1-methyl- and 1-phenylpyrazole, and their corresponding conjugate acids were discussed in terms of reactivity indices. 49 references.

L5 ANSWER 27 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1968:402346 CAPLUS
DOCUMENT NUMBER: 69:2346
ORIGINAL REFERENCE NO.: 69:439a,442a
TITLE: Mass spectra and structure of organic compounds. XXIV. Mass spectra of phenyl derivatives of pyrazole.
AUTHOR(S): Krasnoshchek, A. P.; Khmel'nitskii, R. A.; Polyakova, A. A.; Grandberg, I. I.
CORPORATE SOURCE: Mosk. Gos. Univ. im. Lomonosova, Moscow, USSR
SOURCE: Zhurnal Organicheskoi Khimii (1968), 4(4), 689-95
CODEN: ZORKAE; ISSN: 0514-7492
DOCUMENT TYPE: Journal
LANGUAGE: Russian
OTHER SOURCE(S): CASREACT 69:2346
GI For diagram(s), see printed CA Issue.
AB Mass spectra of the following pyrazoles (I) were obtained [substituent(s), position(s) in I given]: Ph, 1; Ph, 3 (5); Ph, Ph, 1, 3; Ph, Ph, 1, 5; Ph, Ph, 1, 4; Ph, Ph, 3, 5; Ph, Ph, Ph, 1, 3, 5; Ph, Ph, Ph, 3, 4, 5. The stability towards electron impact of I decreased with the number of C-Ph groups and it increased with the number of N-Ph groups. Migrations of Ph groups were observed. A 9-fluorenyl ion (II) was formed from I by an intramol. condensation-elimination mechanism.

L5 ANSWER 28 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1967:516333 CAPLUS
DOCUMENT NUMBER: 67:116333
ORIGINAL REFERENCE NO.: 67:21890h,21891a
TITLE: 1,3-Dipolar cycloadditions. XXXIII. Differences in the reactivity of substituted nitrilimines
AUTHOR(S): Huisgen, Rolf; Adelsberger, Klaus; Aufderhaar, Ernst; Knupfer, Hans; Wallbillich, Guenter
CORPORATE SOURCE: Univ. Munich, Munich, Fed. Rep. Ger.
SOURCE: Monatshefte fuer Chemie (1967), 98(4), 1618-50
CODEN: MOCHAP
DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 67:116333
GI For diagram(s), see printed CA Issue.
AB cf. CA 67: 99380s. Disubstituted nitrilimines (16), released from hydrazide halides with Et3N were compared in their ability to undergo cycloaddns. with 12 dipolarophiles of various activities. Electron-attracting substituents on the nitrilimine C and N stabilized the ground state, reduced the 1,3-dipolar activity, and promoted the formation of tetrasubstituted 1,4-dihydro-1,2,4,5-tetrazines (I). At least 3

different reaction paths from hydrazide halides to 1,4-dihydrotetrazines were shown.

L5 ANSWER 29 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1966:67089 CAPLUS
DOCUMENT NUMBER: 64:67089
ORIGINAL REFERENCE NO.: 64:12503b-c
TITLE: Pyrazoles. LIII. Ultraviolet and fluorescence spectra of some phenylpyrazoles. Ortho effect of substituents in position 5
AUTHOR(S): Grandberg, I. I.; Tabak, S. V.; Kost, A. N.
CORPORATE SOURCE: M. V. Lomonosov State Univ., Moscow
SOURCE: Khimiya Geterotsiklicheskikh Soedinenii (1965), (6), 901-4
CODEN: KGSSAQ; ISSN: 0132-6244
DOCUMENT TYPE: Journal
LANGUAGE: Russian
AB cf. CA 64, 0704c. Uv absorption spectra in MeOH of 1-phenylpyrazoles substituted in position 5 differed from derivs. substituted in positions 3 and 4 by hypsochromic shifts with hypochromic effect. This fact was explained by the effect of both electron-donor and electron-acceptor substituents in position 5 of pyrazole on the phenyl ring. The coplanarity of the phenyl and pyrazole rings violated the ortho effect. The groups increasing the steric effect were found in the order: Ph < OH equal or nearly equal to NH2 < Cl < NHAc < Me < CO2H. Analysis of the fluorescence spectra proved this fact. 19 references.

L5 ANSWER 30 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1964:432381 CAPLUS
DOCUMENT NUMBER: 61:32381
ORIGINAL REFERENCE NO.: 61:5631g-h,5632a
TITLE: Reactions of phenyl-substituted heterocyclic compounds. V. Nitrations of 1,3- and 1,5-diphenylpyrazoles
AUTHOR(S): Lynch, Brian M.; Hung, Yuk-Yung
CORPORATE SOURCE: St. Francis Xavier Univ., Antigonish
SOURCE: Canadian Journal of Chemistry (1964), 42(7), 1605-15
CODEN: CJCHAG; ISSN: 0008-4042
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 61:32381
GI For diagram(s), see printed CA Issue.
AB cf. CA 59, 10053c. Dinitration of 1,3- or 1,5-diphenylpyrazole in H2SO4 gave the corresponding bis(p-nitrophenyl) compds. (I) and (II), while HNO3-Ac2O gave the 4-nitro-1-(p-nitrophenyl)-compds. (III and IV). Mononitration at the 4-position occurred when the diphenylpyrazoles and several other 1-phenyl-pyrazoles were nitrated at 0° by HNO3-Ac2O. Possible explanations of the dependence of orientation on the nature of the nitrating agent were discussed. Nuclear magnetic resonance (n.m.r.) spectroscopy was used in demonstrating the structures of many of the nitration products, and a general discussion of the n.m.r. spectra of substituted 1-phenylpyrazoles was given.

L5 ANSWER 31 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1963:408935 CAPLUS
DOCUMENT NUMBER: 59:8935
ORIGINAL REFERENCE NO.: 59:1616a-c
TITLE: Pyrazoles. XXXIV. Ultraviolet spectra of pyrazole systems
AUTHOR(S): Grandberg, I. I.
CORPORATE SOURCE: M. V. Lomonosov State Univ., Moscow
SOURCE: Zhurnal Obshchei Khimii (1963), 33, 519-25

CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB Ultraviolet spectra are reported for 117 substituted pyrazoles. Halogen atoms, alkyl, or NH2 groups produce a small bathochromic effect on the K band of pyrazole; in the presence of only these auxochromes the band is below 235 mμ; chromophores such as aryl groups, NO2, or NO groups, caused a shift of the K band to 242-80 mμ. The largest bathochromic shift occurs with auxochromes in 1- and 4-positions. If the group interaction between these substituents and the ring occurs through p-electrons, the bathochromic shift is small. Estimation of electron mobilities of heterocyclic rings on the basis of bathochromic band shifts resulted in the following series of ascending magnitude of the shift: 2-selenophene-yl, 2-thienyl, 2-furyl, Ph. The ferrocenyl radical as a substituent on the pyrazole ring acts as a typical auxochrome and does not conjugate with the pyrazole ring. Cf. CA 58,3290f.

L5 ANSWER 32 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1963:402891 CAPLUS
DOCUMENT NUMBER: 59:2891
ORIGINAL REFERENCE NO.: 59:414e-g
TITLE: Reactions of phenyl-substituted heterocyclic compounds. II. Nitrations and brominations of 1-phenylpyrazole derivatives
AUTHOR(S): Khan, Misbahul Ain; Lynch, Brian M.; Hung, Yuk-Yung
CORPORATE SOURCE: Mem. Univ. Newfoundland, St. John's
SOURCE: Canadian Journal of Chemistry (1963), 41, 1540-7
CODEN: CJCHAG; ISSN: 0008-4042
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB Nitrations of 1-phenylpyrazole (I, R = H) (II) 1-p-biphenylylpyrazole (III) and 1,5-diphenylpyrazole by acetyl nitrate (nitric acid-acetic anhydride) occur selectively in the 4-position of the pyrazole ring, as do brominations of II and III in CHCl3. These results are in agreement with Brown's calcns. (CA 49, 8642g) of localization energies for electrophilic substitution in pyrazole. II, e.g., gives I (R = NO2). However, nitration of II by mixed acids at 12° yields 1-p-nitrophenylpyrazole, and bromination of II by Br in concentrated H2SO4 in the presence of Ag2SO4 yields 1-p-bromophenylpyrazole. The variations in orientation of substitution can be rationalized if the reacting species of I in strongly acidic solvents is the conjugate acid, in which the pyrazole ring is deactivated by protonation. Cf. CA 58, 6819f.

L5 ANSWER 33 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1960:2188 CAPLUS
DOCUMENT NUMBER: 54:2188
ORIGINAL REFERENCE NO.: 54:505b-e
TITLE: Pyrazoles. II. Synthesis of N-phenylpyrazoles from corresponding pyrazolines
AUTHOR(S): Grandberg, I. I.; Kost, A. N.
CORPORATE SOURCE: State Univ., Moscow
SOURCE: Zhurnal Obshchei Khimii (1959), 29, 658-62
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 54:2188
AB cf. C.A. 53, 10188f. Adding over 1.5 hrs. of 58 g. CH2:CHCHO and 108 g. PhNHNH2 to 400 ml. Et2O at 5-10°, stirring 5 hrs., evaporating the solvent, adding 300 ml. 2N H2SO4 and steam distilling gave 30% N-phenylpyrazoline, b14 143-6°, n20D 1.6156, d20 1.0984. This (29.2 g.) refluxed gently 1 hr. with 6.4 g. S gave 76% 1-phenylpyrazole,

b6 106-9°, b10 124°, b30 141-2°, 1.5976, 1.0908. Similarly were obtained: 61% 1-phenyl-3-methylpyrazole, b19 139-40°, m. 38°; 88% 1,3-diphenylpyrazole, m. 85°; 84% 1,5-diphenylpyrazole, b8 182-3°, m. 56°. Heating 0.5 hr. 20.8 g. benzalacetophenone with 10.8 g. PhNHNH2 in 15 ml. EtOH and 15 ml. C6H6 (if an exothermic reaction failed to occur, 2 drops HCO2H was added), the solvents removed and the residue heated 1 hr. with 3.1 g. S as above yielded 67% 1,3,5-triphenylpyrazole, m. 140°. Similarly were obtained: 60% 1-phenyl-3-tert-butylpyrazole, b18 151°, m. 74°; 87% 1-phenyl-3-acetamidopyrazole, m. 128°; and 39% 1-phenyl-3-aminopyrazole, b8 167-70°, m. 90° (picrate, m. 158-9°) (Duffin and Kendall, C.A. 49, 10269c).

L5 ANSWER 34 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1948:25374 CAPLUS
DOCUMENT NUMBER: 42:25374
ORIGINAL REFERENCE NO.: 42:5450f-i,5451a-i,5452a-i,5453a-d
TITLE: Heterocyclic syntheses. IX. Ketone reagents and anils of hydroxymethylene ketones
AUTHOR(S): Panizzi, Luigi; Monti, Elios
CORPORATE SOURCE: Ist. chim. generale anal. politec., Milan, Italy
SOURCE: Gazzetta Chimica Italiana (1947), 77, 556-71
CODEN: GCITA9; ISSN: 0016-5603
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 42, 903h. Whereas NH2OH.HCl (I) and PhNHNH2 (II) react with both the CO and the CHOH group of RCOCH:CHOH compds., and form 3- and 5-substituted isoxazoles and pyrazoles, with RCOCH:CHOR' (III) compds. the reaction is confined to the CO group, whereby only 3-substituted heterocyclic derivs. are formed (cf. P. and Sbrillo-Siena, C.A. 41, 1221d). The present work describes a method for preparing exclusively the corresponding 5 substituted derivs., viz., by making I and II react with RCOCH:CHNHPh (IV) compds. In each case PhNH2 (V) and water are evolved, and cyclization then takes place. The IV structure is preferred to the RCOCH2CH:NPh (VI) structure because it is in better accord with the notable stability to heat, acids, and alkalies, with the formation of similar compds. from secondary anilines, and with spectrochem. measurements of analogous imino-enol-amine systems. However, if the compds. react also in the VI form, the mechanism is probably: A comparison of this reaction with that of III compds., in which tautomerism is impossible, indicates that the presence in IV of the N and of a mobile amino-H has a decisive role in the course of the reaction. The problem should be resolved by the behavior of ketone derivs. formed from hydroxymethylene ketones and secondary amines, where again tautomerism would be impossible. HCO2Et (22 g.) and 14.5 g. acetone, added slowly to a suspension of 5.7 g. powdered Na in 120 cc. anhydrous C6H6, allowed to stand several hrs. at 30-40°, agitated with ice-water, the aqueous layer treated with excess V in AcOH, the orange-brown oil which seps. extracted with C6H6, the extract dried by CaCl2, evaporated, and distilled in vacuo, and the fraction (13 g.) which b12 148-50° allowed to solidify, washed with ligroin, and purified by C6H6-ligroin, yields acetylacetaldehyde anil, AcCH:CHNHPh (VII), m. 50-2°; FeCl3 turns its alc. solns. red. Alc.VII (1 g. in 5 cc.) and 0.65 g. I in a min. of water, refluxed 1.5 hrs., diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract distilled, the fraction at 50° agitated with saturated aqueous CdCl2, and the addition product washed with EtOH and Et2O, dried, and distilled twice, yield 0.3 g. of 5-methylisoxazole (VIII). VIII (0.24 g.) and EtONa (from 0.1 g. Na and 1.5 cc. anhydrous EtOH), allowed to stand, diluted with water, 0.55 g. p-O2NC6H4NHNH2 (IX) in 3 cc. glacial AcOH added, then NaCl, allowed to stand 1 hr., filtered, and washed with water, yield

p-O2NC6H4NHN:CMeCH2CN, m. 183-5° (cf. Justoni, C.A. 35, 5110.8). VII (1 g.), 0.71 g. II, 0.65 cc. concentrated HCl, and 10 cc. EtOH, refluxed 3 hrs., diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract evaporated, the residue steam-distilled, the oil distillate extracted with Et2O, and the extract dried by Na2SO4 and distilled, leave a residue of PhN.N:CH.CH:CMe. Its chloroplatinate m. 193-6° (decomposition) (cf. Ber. 32, 2891(1899); Stoermer, C.A. 1, 1287), and its picrate m. 93-7° (cf. Ber. 32, 2891(1899); Stoermer, loc. cit.). Alc. VII (0.5 g. in 10 cc.), 1 g. NaOAc, and p-O2NC6H4N2Cl (X) (from 0.5 g. IX), allowed to stand, and the precipitate purified by BuOH, yield (p-nitrophenylazo)acetylacetaldehyde anil, AcC(:CHNHPh)N:NC6H4NO2-p (XI), orange, m. 186-8° (decomposition); NaOH turns its alc. solns. intense red. An alc. suspension of XI (1 g. in 110 cc.) and 0.26 g. I, refluxed 3 hrs., allowed to stand, and the precipitate purified by BuOH, yield (p-nitrophenylazo)acetylacetaldehyde oxime, p-O2NC6H4N:NCHAcC(:NOH)H, orange-red, m. 221-3° (decomposition). Alc. VII (1 g. in 15 cc.), 1.8 g. NaOAc, and PhN2Cl (from 0.6 g. V), allowed to stand and the precipitate purified by EtOH, yield (phenylazo)acetylacetaldehyde anil (XII), yellow, m. 128-30°. XII (0.5 g.), 15 cc. glacial AcOH, and 0.2 g. II, heated 1.5 hrs. on a steam bath and allowed to stand, precipitate the hydrazone, AcCH(N:NPh)CH:NNHPh, golden yellow, m. 215-18°. The mother liquor, diluted, allowed to stand, and the precipitate purified by MeOH, yields PhN.CH:CH.C(N:NPh):CMe, m. 108-11°. PhAc (24 g.) and 14 g. HCO2Me, added slowly to a suspension of 5 g. powdered Na in 100 cc. anhydrous C6H6 (the reaction is energetic and must be cooled), allowed to stand, ice water added, a small excess of V.AcOH added to the aqueous layer, and the precipitate purified by BuOH, yields 36 g. BzCH:CHNHPh (XIII), lemon-yellow, m. 140-1° (cf. Claisen and Fischer, Ber. 21, 1137(1888)). Alc. XIII (4 g. in 20 cc.) and 1.9 g. I in a min. of water, heated 1 hr. at 100°, most of the EtOH evaporated, diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract dried by Na2SO4, evaporated, and the residue (2.5 g.) fractionally distilled, yield 5-phenylisoxazole (XIV), b3-4 110° (cf. Claisen, Ber. 36, 3671(1909)). XIV (0.496 g.) and EtONa (from 0.35 g. Na and 5 cc. anhydrous EtOH), heated a short time at 40-50°, excess IX in AcOH added, allowed to stand overnight, and the precipitate washed and purified by BuOH, yield α-cyanoacetophenone p-nitrophenylhydrazone, p-O2NC6H4NHN:CPhCH2CN, yellow, m. 177-8°. XIII (3 g.), 1.74 g. II, 1.5 cc. concentrated HCl, and 40 cc. EtOH, refluxed 2 hrs., most of the EtOH evaporated, diluted with water, acidified with HCl (Congo red), extracted with Et2O, the extract evaporated, and the oil (2.6 g.) purified by distillation in vacuo, yield PhN.N:CH.CH:CPh (cf. Claisen and Fischer, loc. cit.). Reduction by Na and EtOH yields PhN.N:CH.CH2.CHPh, m. 133-5° (cf. Ber. 26, 112(1893)). XIII (3 g. in 300 cc. MeOH), excess NaOAc, and X (from 1.9 g. p-O2NC6H4NH2), allowed to stand, and the precipitate purified by BuOH, yield (p-nitrophenylazo)benzoylacetaldehyde anil (XV), orange-red, m. 202-3°. XV (0.46 g.) and 0.1 g. I in 50 cc. EtOH, refluxed 1.5 hrs., evaporated, diluted with water, and the precipitate purified by BuOH, yield (p-nitrophenylazo)benzoylacetaldehyde oxime, m. 209-12°. Alkalies turn its alc. solns. orange-red. XIII (1 g.) in 150 cc. MeOH, 1.5 g. NaOAc, and PhN2Cl (from 0.5 g. V), allowed to stand, and the precipitate (0.3 g.) purified by EtOH, yield (phenylazo)benzoylacetaldehyde anil (XVI), orange-yellow, m. 137-9°. XVI (0.22 g.), 0.07 g. II, and 15 cc. glacial AcOH, heated 2 hrs. at 100°, diluted with water, partially neutralized, and the precipitate (0.17 g.) purified by EtOH, yield 1,5-diphenyl-4-phenylazopyrazole, PhN.CH:CH.C(N:NPh):CPh, yellow, m. 117-18°. PhCH:CHAc (7.3 g.), 4

g. HCO2Me, and a suspension of 1.25 g. powdered Na in 60 cc. anhydrous C6H6 react energetically and the mixture must be cooled; the product, allowed to stand, agitated with ice-water, excess V.AcOH added to the aqueous layer, and the precipitate purified by EtOH, yield approx. 20% of cinnamoylacetaldehyde anil, PhCH:CHCOCH:CHNHPh (XVII), yellow, m. 150-1°. XVII (2 g.) and 0.8 g. I in 25 cc. EtOH, refluxed 2 hrs., concentrated to a small volume, diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract evaporated, the residue steam-distilled, the distillate allowed to solidify, and purified by petr. ether, yield 5-styrylisoxazole, O.N:CH.CH:CCH:CHPh (XVIII), m. 42-3°; its acetone solution decolorizes KMnO4; its AcOH solution decolorizes Br slowly. By treatment with cold EtONa solution, dilution with water, acidification, and purification by CCl4, XVIII forms cinnamoylacetonitrile, PhCH:CHCOCH2CN, m. 95-8°. With excess IX in AcOH, it ppts. the p-nitrophenylhydrazone, m. 210-12° (cf. Musante, C.A. 37, 2737.5). XVIII (2 g.), 0.95 g. II, 0.85 cc. concentrated HCl, and 15 cc. EtOH, refluxed 2 hrs., concentrated to a small volume, diluted with water, extracted with Et2O, the extract evaporated, the residue distilled in vacuo, and the distillate, b15-20 230°, allowed to solidify and purified by EtOH, yield 1-phenyl-5-styrylpyrazole (XIX), m. 127°, soluble in aqueous HCl. (NH4)2Cr2O7 (1.5 g.), added slowly to 0.8 g. XIX in 20 cc. boiling 20% H2SO4, extracted with Et2O, the extract evaporated, the residue taken up in aqueous Na2CO3, extracted with Et2O, the aqueous residue acidified with HCl, extracted with Et2O, the extract evaporated, and the residue heated at 110° (to remove BzOH) and purified by boiling water, yields 0.2 g. 1-phenyl-5-pyrazolecarboxylic acid, PhN.N:CH.CH:CCO2H, m. 179-81°. X (from 0.3 g. p-O2NC6H4NH2), added to 0.5 g. XVII in 50 cc. MeOH and 1 g. NaOAc, and the precipitate (0.5 g.) purified by BuOH, yields (p-nitrophenylazo)cinnamoylacetaldehyde anil (XX), orange, m. 161-3°. XX (0.4 g.) in 50 cc. EtOH and 0.1 g. I, refluxed 2 hrs., concentrated to a small volume, and the residue allowed to solidify and purified by BuOH, yield (p-nitrophenylazo)cinnamoylacetaldehyde oxime, PhCH:CHCOCH(N:NC6H4NO2-p)C(:NOH)H, yellow, m. 194°. XVII (1 g.), 1.2 g. NaOAc, and PhN2Cl (from 0.4 g. V) in 100 cc. MeOH, allowed to stand 1 hr., and the precipitate purified by BuOH, yield (phenylazo)cinnamoylacetaldehyde anil (XXI), red, m. 148-9°. Alc. XXI (0.25 g. in 50 cc.), 0.1 g. II, and 0.1 cc. concentrated HCl, boiled a short time, allowed to stand, and the precipitate purified by BuOH, yield the phenylhydrazone, C23H20ON4, orange-yellow, m. 215-16°. When heated cautiously in vacuo, and the distillate purified by EtOH, it yields 1-phenyl-4-phenylazo-5-styrylpyrazole, yellow, m. 158-60°; a trace turns concentrated H2SO4 intense cherry-red. To study IV compds. in which R is Me2C:CH-, Me2C:CHCOCH2CHO (XXII) was made to react with V.AcOH with the intention of obtaining Me2C:CHCOCH:CHNHPh. However, the reaction was different and an isomer was obtained. Me2C:CHAc (20 g.), 16 g. HCO2Me, 100 cc. anhydrous C6H6, and MeONa (from 4.9 g. Na), kept below 10° overnight, agitated with ice-water, the aqueous layer treated with V.AcOH, the brown-red oil extracted with C6H6, the extract evaporated, the residue distilled in vacuo, the orange-red fraction, which b14 150-200°, allowed to partially solidify, filtered, and washed with ligroin, and the residue (6.5 g.), purified by CCl4, yields 1-phenyl-2,3-dehydro-6,6-dimethyl-4-piperidone, HC:CH.CO.CH2.CMe2.NPh (XXIII), m. 132°, soluble in dilute HCl (repptd. unaltered by alkalies); its CS2, solution absorbs Br; it does not immediately decolorize KMnO4 in acetone. XXIII (0.5 g.) in 5 cc. MeOH and 0.26 g. I, refluxed 3 hrs.,

diluted with water, extracted with Et2O, the aqueous layer made alkaline with NaOH, and
the green-yellow precipitate (0.3 g.) purified by animal charcoal and ligroin, yield the oxime, HC:CH.C(:NOH).CH2.CMe2.NPh, m. 167-9°, soluble in dilute HCl (repptd. by alkalies). XXIII (0.5 g.), 1 g. NaOAc, and p-O2NC6H4N2Cl (from 0.35 g. p-O2NC6H4NH2) give 0.5 g. of a precipitate which, purified by EtOH, yields the p-nitrophenylazo derivative, HC:CH.CO.CH2.CMe2.NC6H4N:NC6H4NO2-p (XXIV), carmine-red, m. 170°; its alc. solns. turn orange-red with NaOH. The constitution of XXIV seems, in view of the similarity between XXIII and dialkylanilines, more probable than that of a derivative formed by coupling on the piperidone nucleus.

L5 ANSWER 35 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1945:12004 CAPLUS
DOCUMENT NUMBER: 39:12004
ORIGINAL REFERENCE NO.: 39:1871c-g
TITLE: Heterocyclic syntheses. IV. New isoxazole- and pyrazolecarboxylic acids
AUTHOR(S): Panizzi, Luigi
SOURCE: Gazzetta Chimica Italiana (1943), 73, 13-23
From: Chem. Zentr. 1944, I, 424-5.
CODEN: GCITA9; ISSN: 0016-5603
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 38, 5500.2. BzCH2CO2Et, HC(OEt)3 and Ac2O give Et (ethoxymethylene)benzoylacetate (I), light yellow oil, b8-10 192-5°; warming with FeCl3 gives a red color. I with absolute EtOH-KOH in ether at 0° gives Et (hydroxymethylene)benzoylacetate, yellow, b3-4 135-6° (partial decomposition). I and NH2OH in EtOH, boiled 2 hrs., give the Et ester (II), b45 142-3°, of 5-phenyl-4-isoxazolecarboxylic acid (III), O.N:CH.C(CO2H):CPh, m. 155-6° (prepared from the ester with 1:1 HCl). The structure of III follows from the reaction of II with boiling alc. KOH or with cold EtONa to give Et benzoylcyanoacetate, m. 40-1°. I and PhNHNH2 in AcOH give the Et ester, m. 112.5-14°, of 1,5-diphenyl-4-pyrazolecarboxylic acid (IV), N:CH.C(CO2H):CPh.NPh, m. 180° (decomposition); decarboxylation of IV yields 1,5-diphenylpyrazole, which was reduced by EtONa to the pyrazoline, m. 135-6°. The positions of the Ph groups in III and IV are taken as proof that NH2OH and PhNHNH2 add to the double bond and not to the CO group; ring formation follows through the loss of EtOH and H2O. Et phenylpyruvate (m. 45°) yields with HC(OEt)3 and Ac2O Et (ethoxymethylene)phenylpyruvate, b3-4 171-2°; the free acid (V) m. 124°. V and NH2OH in EtOH give a compound (VI) [assumed to be PhCH(COCO2Et)CH(OEt)NHOH], thick reddish oil, b3-4 155-8° (partial decomposition); the alkali solubility and FeCl3 reaction indicate an enol form; with
20% KOH VI gives a small yield of 4-phenyl-5-isoxazolecarboxylic acid, m. 158° (decomposition); the Et ester (an oil) and EtONa give PhCH(CN)COCO2Et(?), which was not characterized. V and PhNHNH2 yield an amorphous product which with alkali gives 1,4-diphenyl-3-pyrazolecarboxylic acid, m. 227-8°.

L5 ANSWER 36 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1941:17981 CAPLUS
DOCUMENT NUMBER: 35:17981
ORIGINAL REFERENCE NO.: 35:2891b-f
TITLE: Transformation of 3-isoxazolecarboxylic acids into pyrazole derivatives. IV
AUTHOR(S): Cusmano, Sigismondo

SOURCE: Gazzetta Chimica Italiana (1940), 70, 227-35
CODEN: GCITA9; ISSN: 0016-5603
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB cf. C. A. 34, 7903.8. The transformation of 3-isoxazolecarboxylic acids into pyrazolonimines by fusion with PhNHNH2 may proceed by decarboxylation followed by ring closure of the resulting cyano ketone phenylhydrazone. To test this hypothesis the fusion was repeated in the presence of Natur Kupfer C (I) (or ordinary reduced Cu) so that, at the lower decarboxylation temps. it might be possible to isolate the phenylhydrazone prior to ring closure and so shed some light on the mechanism of the reaction. A mixture of 1 g. of 5-phenyl-3-isoxazolecarboxylic acid (II), 1 g. I and 1 g. PhNHNH2 in 20 cc. alc. was boiled for a few min. over a free flame, filtered, alkalinized with Na2CO3, extracted free from PhNHNH2 with ether, acidified with dilute H2SO4, and extracted with ether. The residue from the evaporated extract gave 1,5-diphenyl-3-pyrazolecarboxylic acid (III), m. 185° (Et ester, m. 98°), decarboxylated by fusion to give 1,5-diphenylpyrazole, m. 55°, and identical with the known acid prepared by the action of PhNHNH2 on BzCH2COCO2H. A similar transformation of 5-methyl-3-isoxazolecarboxylic acid (IV) gave 1-phenyl-5-methyl-3-pyrazolecarboxylic acid, m. 136° (Me ester, m. 55°), decarboxylated to 1-phenyl-5-methylpyrazole, transformed into the known picrate, m. 98°. In these transformations alc. can be replaced by other solvents. In the absence of I or in the presence of PhNH2 instead of PhNHNH2 the isoxazolecarboxylic acid is recovered unchanged.

L5 ANSWER 37 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1927:11948 CAPLUS
DOCUMENT NUMBER: 21:11948
ORIGINAL REFERENCE NO.: 21:1450c-h
TITLE: Reaction of hydrazine with hydroxymethylene ketones and their derivatives
AUTHOR(S): v. Auwers, K.; Mauss, H.
SOURCE: Justus Liebigs Annalen der Chemie (1927), 452, 182-210
CODEN: JLACBF; ISSN: 0075-4617
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB BzCH:CHONa(I) and PhNHNH2 give a crude product, m. 110-2°, which, recrystd. from C6H6 and EtOH, gives 2-[β-benzoylvinyl]-1-phenylhydrazine (II), m. 129.5-30.5°; heating at 185-7° and 14 mm. gives 1,5-diphenylpyrazole (III), m. 55-6°; the mother liquor gives a mixture of III and the 1,3-di-Ph derivative (IV). Attempts to benzoylate II gives only III. II does not react with I; it is oxidized by FeCl3 but the only product isolated was III; II in EtOH-NaOH, shaken with air, gives β-[benzoylvinyl]azobenzene, red, m. 50-60°. I and PhNHNH2 in EtOH at room temperature for 2-3 days give PhNHNHCHO (V), m. 141.5-25°, pale yellow crystals, m. 146-7°; II, the azo derivative and BzMe. Crystallizing II from Me2CO, AcOEt or C6H6 gives the isomeric 1-[β-benzoylvinyl]-1-phenylhydrazine (V), m. 164°while mother liquor gives IV. II or V and p-O2NC6H4NHNH2 in C5H5N for 2 hrs. at room temperature give the compound BzCH:CHNPhNHCOC6H4NO2, yellow, m. 205°. Oxidation of II or VI with KMnO4 in Me2CO gives BzCH:CHNHPh. Condensation of II or VI with p-O2NC6H4CHO gives the p-nitrobenzal derivative of VI, yellow, m. 173-4°, also obtained from BzCH:CHOH and p-O2NC6H4CH:NNHPh. BzCH:CHOH and V in EtOH, heated 2 hrs., give the α-phenyl-β-formylhydrazidc of hydroxymethylacetophenone, yellow, m. 148-9°; heated with 2 N HCl it yields IV. I and p-O2NC6H4NHNH2.HCl in dilute EtOH give the p-nitrophenylhydrazide, orange-yellow, m. 156-7°; heating with AcOH about 0.25 hr. gives 1-[P-Nitrophenyl]-5-phenylpyrazole (VII), b14 240-2°, m. 117-8°; this also results from p-O2NC6H4NHNH2 and

BzCH:CHOBz. The p-amino derivative, m. 148.5-9.5°; the diazo compound treated with SnCl2 and NaOH, gives III. When BzCH:CHOBz and p-O2NC6H4NHNH2 in PrOH are allowed to stand 1 day there results some VII and the bis-p-nitrophenylhydrazine derivative, orange-red, m. 195-200°, crystallizing with 1 Me2CO; heating on the H2O bath gives 1-[p-nitrophenyl]-3-phenylpyrazole (VIII), yellow, m. 169-9.5°. 1-[p-Nitrophenyl]-3-phenyl- pyrazol-5-one, brownish, m. 202-3°; attempted reduction with PBr3, resulted in complete decomposition Nitration of VIII or IV gives the same dinitro derivative, m. 226-8°. BzCH:CHNHNMeCH:CHBz, m. 137.5-8.5°, and Me2SO4 give a di-Me derivative, m. 175-6°, decomposed by heating with mineral acid or alkali; the neutral product is C6H3BZ3, m. 119-20°. The di-Me derivative was obtained from I and (NHMe)2.2HCl in HCl. 1-Methyl-1-[benzoylvinyl]-2-[p-nitrobenzal]hydrazine, yellow, m. 207°.

L5 ANSWER 38 OF 38 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1925:15752 CAPLUS
DOCUMENT NUMBER: 19:15752
ORIGINAL REFERENCE NO.: 19:2048f-i,2049a-g
TITLE: Isomerism relationships in the pyrazole series. II. 3(5)-Phenylpyrazole and its derivatives
AUTHOR(S): v. Auwers, K.; Schmidt, W.
SOURCE: Berichte der Deutschen Chemischen Gesellschaft [Abteilung] B: Abhandlungen (1925), 58B, 528-43
CODEN: BDCBAD; ISSN: 0365-9488
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 19:15752
GI For diagram(s), see printed CA Issue.
AB cf. C. A. 18, 1296. Unlike the dialkylpyrazoles, of which the 1,5-forms are incapable of existence, the C-phenylalkylpyrazoles can exist in both the 1,3- and 1,5-forms. While it might be concluded from this that the non-existence of the 1,5-dialkyl derivs. is due, as had been tentatively suggested, to a mutual repulsion of the electrochem. similar radicals, the relationships are not so simple as all this and further data will be necessary before the phenomena can be explained. Both 1,3- (I) and 1,5-diphenylpyrazole (II) are stable and their structures have been determined with certainty, but Claisen and Fischer from HOCH: CHCOPh (III) and Ph2 in Et2O obtained a compound m. 118-20° which on distillation smoothly yielded II (Ber. 21, 1139(1888)) while Knorr and Duden obtained only I (Ber. 27, 109(1893)). v. A. and S. in their own expts. regularly obtained a substance (IV), m. 126°, having the composition of a phenylhydrazone of BzCH2CHO and giving II on distillation in vacuo. The yield of this product, however, was only 25% and the Et2O mother liquor on standing a long time deposited yellowish needles, m. 100-3°, which on distillation gave a semi-solid mass from which I was obtained by steam distillation In the action of PhNHNH2 on III, therefore, there are formed both of the possible hydrazones BzCH2CH:NNHPh (IV) and PhC(:NNHPh)CH2CHO, which explains the apparent discrepancy between the results of C. and F. and of K. and D. BzCH:CHOBz (V), BzCH:CHOCO2Et (VI) or BzCH:CHOEt (VII) treated with PhNHNH2 regularly lost the radical attached to the O, even under the mildest conditions, yielding a product C16H14ON2 (VIII), m. 162°, which is readily converted into I but does not give PhNH2 with Na-Hg and AcOH in alc., is insol. in alkalies and does not show aldehyde reactions; it is provisionally assigned the structure PhN.N:CPh.CH2.CHOH. When it is treated in C5H5N with ClCO2Et a H atom is replaced by CO2Et and the resulting ester (IX) is readily hydrolyzed. In preparing VIII, the crude product frequently m. around 115-20° but a single crystallization sufficed to raise the m. p. to 162°; v. A. and S. think it likely that the low melting product is a labile form of VIII. VIII smoothly yields I when warmed a very short time with glacial AcOH or kept 5 min. in it in the

cold or when warmed a short time with alc. and a couple drops of HCl or when boiled in Me2CO, while IV is converted into II only on long boiling in glacial AcOH or dilute alc. HCl or on distillation, indicating that of the 2 isomers I has the greater tendency to be formed. 3(5)-Phenylpyrazole (X) with MeBr in a sealed tube or with Me2SO4 gives a mixture of chiefly 1-methyl-3-phenylpyrazole (XI) and the 1,5-isomer (XII). XII was also prepared (1) quant. by condensing PhCH:CBrCHO with MeNHNH2 and treating the resulting yellow oily bromopyrazoline with NaOAc, and (2) from the Na salt of III, (MeNHNH2)2. H2SO4 and NaOAc in H2O or free HI and MeNHNH2 in Et2O and treatment of the resulting compound (XIII), (CH:CHBz)2NNHMe, with hot glacial AcOH or boiling dilute alc. HCl; in the last case there is formed a mixture of XI and XII in which XII predominates. V with MeNHNH2 gives chiefly XI but also some XII. While according to Wenglein (Diss. Jena, 1895) the methiodide (XIV) obtained from either XI or XII gives only XI on heating, v. A. and S. find that in fact it gives only 32% XI and 68% XII. Ethylation of X with a large excess of EtBr gives only 1 compound (XV), the comparison of whose consts. with those of XI and XII shows clearly that it is 1-ethyl-3-phenylpyrazole. The Na salt of III is obtained in 90% yield (crude product of varying degrees of purity) from 11.5 g. Na wire under cold C6H6 slowly treated with 60 g. MeCOPh and 55 g. acid-free HCO2Et. Bz derivative (V) of III (70% from III and BzCl in C5H6N), m. 75-5.5°, unchanged by glacial AcOH or alc. HCl. Et β-benzoylvinyl carbonate (VI) (80% from III and ClCO2Et in cold C5H5N), m. 57-9°. Et β-benzoylvinyl ether (VII), b10 162-3°. Carboxyethyl derivative (IX) of VIII, m. 156°, rapidly hydrolyzed by dilute H2SO4 even in ice. X, b11 177-8°, b. 313-4°, m. 79°, d499.6 1.0818, n 1.58166, 1.58890, 1.60734 for α, He and β at 100.8°, EΣ 1.09, 1.15, 31% for α, D and β-α. Treated in cold dilute H2SO4 with NaNO2 it gives a yellow oil whose Et2O solution soon deposits the nitrate of X, m. 126° (decomposition). N-Ac derivative, b10 157-8°, m. 64-5°. Methiodide of I, m. 172°, regenerates I when heated above its m. p. Methiodide of II, m. 207°, yields II above its m. p. XI m. 55-6°, b12 145-6°, d499.6 1.0232, n 1.55539, 1.56216, 1.57982 for α, He and β at 100.8°, EΣ 1.27, 1.33, 37% for α, D and α-β. XIIb10 127°, d416.8 1.0946, n 1.58350, 1.58999, 1.60653, 1.62148 for α, He, β and γ at 15.8°, EΣ 0.40, 0.42, 19%, 19% for α,D,β-α and γ-α. Picrate, greenish yellow, m. 143-4°.

α-Methyl-β, β-bis-[β'-benzoylvinyl]hydrazine (XIII), yellow, m. 137.5-8.5°, insol. in dilute HCl, soluble (but with rapid alteration) in concentrated acid with golden yellow color.

1-Methyl-3-phexyl-4-bromopyrazole (90% from XI and Br in AcOH), b12 175-6°, d418.9 1.4707, n 1.61025, 1.61711, 1.63442, 1.65050 for α, He, β and γ at 18.9°, EΣ 0.27, 0.29, 20%, 22% for α, D, β-α and γ-α.

1-Methyl-5-phenyl-4-bromopyrazole b12 155-6°, m. 63-4° and if quickly cooled if m. 65-6° but if cooled slowly it again m. 53-4°, d456.6 1.4199, n 1.58179, 1.58790, 1.60325, 1.61706 at 57.6°, EΣ 0.20, 0.22, 13%, 13%. Methylation of the 4-Br derivative of X with alkaline Me2SO4 gives a mixture of the 2 above compds. XV b12 152-3°, m. 36.5-7.5°, d411.6 1.0667, n 1.58209, 1.58897, 1.60657, 1.62283 at 11.6°, EΣ 0.92, 0.98, 34%, 36%.

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